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Variational treatment of electron degradation and yields of initial molecular species

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We present a general theory of electron degradation and of the yields of initial species such as ions and excited states that appear in matter as a result of irradiation with electrons. We give variational expressions for observable quantities such as the degradation spectrum, the mean yields, and the yield fluctuations. A systematic analysis using variational principles reveals, in greater detail than ever before, relations among major analytical methods including the Fowler method, the Spencer-Fano method, and the method of Knipp *et al*. Each of these methods represents a different angle of approach to the same problem and leads to the same prediction for the mean yield of any initial species, for a fixed set of electron cross-section data. Among our findings it is noteworthy that the knowledge of the Spencer-Fano degradation spectra for various source-electron energies enables one to calculate by quadrature not only the mean but also the statistical fluctuations of the yield of any initial species. Furthermore, when one introduces small changes in the cross-section data (because of new information or upon consideration of chemical impurities in the medium), one may express the ensuing modifications of any observable quantity in the form of a perturbation expansion. Then, every term in the perturbation series is calculable again from the Spencer-Fano degradation spectra for various source energies *for the unperturbed problem*. In this respect and many others, the Spencer-Fano degradation spectrum is the most basic element in the solution of the degradation problem. Finally, our mathematical analysis of various difference-integral equations (including nonlinear equations) may be of interest in areas other than electron degradation. Therefore, the present paper includes remarks on the physical meaning of adjoint operators and on other points belonging to general mathematical physics.

I. INTRODUCTION

A central problem in the study of matter exposed to high-energy radiations is the determination of the kinds and numbers of initial species formed. Since a substantial fraction of the initial species results from the degradation of electrons ejected within the medium, theoretical attention has been concerned chiefly with electrons as source particles. Always, the problem consists of two interlocking efforts.[1] The first step is the assembly of a complete set of inelastic-scattering cross sections. Our concern in this paper is with the second step, which is often referred to as *bookkeeping*[1] and entails following the course of degradation of the electrons and keeping account of the consequences of all the inelastic events.

There are three general approaches to the bookkeeping portion of the problem that are currently used. The merits of each were previously discussed.[2] One method, machine simulation of either Monte Carlo[3] or "discrete-bin"[4] type, can provide a complete and exact approach to the bookkeeping problem, but as recently emphasized by Bethe and Jacob,[5] further effort is required if general properties such as systematics or scaling laws are sought. The other two methods consist of solution of difference-integral equations.

In the simplest medium consisting of molecules with a single ionization threshold I, the mean number $N_i(T)$ of ions produced in the complete degradation of a source electron of energy T obeys the equation[6]

$$\sigma_{\text{tot}}(T)N_i(T)=\sigma_i(T)+\sum{}_n\sigma_n(T)N_i(T-E_n)$$

$$+\int_I^{(T+I)/2} dE\,\frac{d\sigma_i(T,E)}{dE}$$

$$\times\left[N_i(T-E)+N_i(E-I)\right]. \qquad (1.1)$$

The cross section for excitation of the nth discrete state is $\sigma_n(T)$, and $d\sigma_i(T,E)/dE$ is the differential cross section for production of a secondary electron with kinetic energy $E-I$. The total ionization cross section is

$$\sigma_i(T)=\int_I^{(T+I)/2} dE\,\frac{d\sigma_i(T,E)}{dE}\,,$$

and the total inelastic-scattering cross section is

$$\sigma_{\text{tot}}(T)=\sigma_i(T)+\sum_n\sigma_n(T).$$

Equation (1.1), called the Fowler equation, has a simple meaning: each term on the right-hand side of Eq. (1.1) represents an alternative effect upon $N_i(T)$ of *the next collison* that an electron of energy T undergoes. The first term represents the ion yield due to direct ionization by the source electron. The second represents the yield when the source electron first excites a discrete state, and subsequently (with kinetic energy $T-E_n$) produces an ion. The integral term represents the ionization process in which the primary electron first transfers energy $E>I$ and the two outgoing electrons, with energies $T-E$ and $E-I$, proceed to create additional ion pairs. The faster of these two electrons is conventionally regarded as the primary electron and the slower as the ejected electron. Hence, the upper limit of integration is $\frac{1}{2}(T+I)$. Since $N_i(T)=0$ for $T<I$, Eq. (1.1) can be solved stepwise by *ascending in* T. Similar Fowler equations[7,8] can be written for the average yield $N_s(T)$ of any specific excitation s by replacing N_i in Eq. (1.1) with N_s, and the first term on the right-hand side with $\sigma_s(T)$.

Another approach is the Spencer-Fano[9] method. An elementary account of the theory has been given,[10] and the merit of the method has recently been emphasized.[2] Consequently, the following discussion of the theory is brief.

The Spencer-Fano approach focuses on the energy distribution of all electrons in the medium (i.e., the source electron and the electrons of all subsequent generations), or on a closely related quantity, i.e., the degradation spectrum $y(T_0,T)$. Indeed, Spencer and Fano[9] recognized the key role of the energy distribution (or the flux) in γ-ray and neutron degradation, and extended the idea to the electron-degradation problem. The function $y(T_0,T)\,dT$ represents the total path length of all electrons with energies in the interval $(T,T+dT)$ produced by a unit flux of stationary source electrons of initial energy T_0 and obeys the equation

$$\begin{aligned}\sigma_{\text{tot}}(T)y(T_0,T) &= \sum_n \sigma_n(T+E_n)y(T_0,T+E_n)\\ &\quad+\int_I^\infty dE\,\frac{d\sigma_i(T+E,E)}{dE}\,y(T_0,T+E)\\ &\quad+\int_{2T+I}^\infty dE\,\frac{d\sigma_i(E,T+I)}{dE}\,y(T_0,E)\\ &\quad+\mathfrak{N}^{-1}\delta(T_0-T),\end{aligned} \tag{1.2}$$

where $\mathfrak{N}$ is the number density of molecules in the medium.

Each term on the right-hand side of Eq. (1.2) represents an alternative effect upon $y(T_0,T)$ of *the last collision* that an electron underwent to arrive in the energy interval $(T,T+dT)$. The first term on the right-hand side represents the contributions from all possible discrete excitations in the last collision. The two integral terms represent the contributions from all possible ionization events. It follows from the definition of a secondary electron that the upper limit of the first integral of Eq. (1.2) is actually the lesser of T_0-T and $T+I$. This limit may be extended to infinity with the condition that $d\sigma_i(T,E)/dE=0$ for $T>T_0$. The upper limit of the second integral may also be extended beyond its actual value T_0 with the stipulation $y(T_0,E)=0$ for $E>T_0$.

Throughout this paper we deal with electronic energy losses only. Thus, the cross section $\sigma_n(T)$ refers to electronic excitation whose lowest threshold is E_1. The function $y(T_0,T)$ therefore may be considered as being defined in the domain $E_1\le T\le T_0$ according to Eq. (1.2). (The electron degradation at kinetic energies below E_1 is slower by orders of magnitude and therefore can be regarded as a separate problem.[2]) In certain expressions that appear in our treatment, it is sometimes convenient to stipulate $y(T_0,T)=0$ for $T<E_1$.

The Spencer-Fano equation may be solved stepwise by *descending from* T_0. Once $y(T_0,T)$ is known, the yields of all initial species are determined by simple quadrature as[1]

$$N_s(T_0)=\mathfrak{N}\int_{E_s}^{T_0} dT\,y(T_0,T)\sigma_s(T)\,, \tag{1.3}$$

where E_s is the threshold energy for excitation of the kind s.

The approaches discussed above are exact and require as input a complete set of cross sections. The assembly of input data can be regarded as a separate problem; progress in that area was discussed recently.[11,12]

Our aim in this paper is to consider Eqs. (1.1) and (1.2) as well-defined physicomathematical equations for unknown quantities $N_i(T_0)$ and $y(T_0,T)$ in terms of known cross sections and to seek variational principles for solving these equations. While these variational principles may provide a numerical approach, the main emphasis of the present paper is on the insight provided by these principles into the mathematics and physics of the problem. Our treatment shows that the historically independent approaches through Eqs. (1.1) and (1.2) are closely related to each other. Indeed, they represent *dual modes of description* of the same degradation process. Recall that Eq. (1.1) enumerates different results of the next collision of an electron at energy T, and that Eq. (1.2) enumerates different results of the last collision by which an electron of energy T has appeared. Mathematically, the dual modes of description are expressed by the adjointness, i.e., a notion well known in the transport theory of γ rays[13] and neutrons.[14-16] Section II develops the variational principles for $N_s(T_0)$ and identifies $y(T_0,T)$ as an adjoint function. Section III treats the variational principle for $y(T_0,T)$ and shows that $y(T_0,T)$ itself is an adjoint function. In Secs. IV and V, we consider not only the mean of the yield but also statistical fluctuations around that mean. Although equations describing the fluctuations look more complicated than Eq. (1.1), the variational treatment shows that $y(T_0,T)$ again serves as an adjoint function. Consequently, the degradation spectrum determines not only the mean yield, but also the Fano factor and all other information about the fluctuations.

The basic role of the degradation spectrum is understandable from the following interpretation. The function $y(T_0,T)$ in effect represents the influence of the source term $\mathfrak{N}^{-1}\delta(T_0-T)$ in Eq. (1.2) upon a current value T of the electron energy. Thus, any quantity that characterizes an outcome of the degradation process may be expressed in terms of integrals containing $y(T_0,T)$ over T. In this sense $y(T_0,T)$ plays a role similar to that of the Green's function in mathematical physics in general. In neutron-transport theory, the same idea of the influence of the source particle upon a detector (or observable) property is sometimes called the "importance"[14]; in this language, the Spencer-Fano degradation spectrum is the importance in the electron-degradation problem. This interpretation also explains the usefulness of $y(T_0,T)$ in evaluating effects of small changes in cross-section data upon quantities characterizing an outcome of the degradation process (as we discuss in Sec. VI).

Finally, as a by-product of this investigation, we have developed a compact prescription for the generation of adjoints (or, equivalently, Green's functions or inverses) of integral operators, as discussed in the Appendixes.

For brevity of presentation, we restrict the treatment throughout the present paper to an idealized medium consisting of a single molecular species having a single ionization threshold. For any real medium there are at least three complications: (a) the dissociation of superexcited molecules in competition with preionization, (b) the presence of many ionization thresholds corresponding to different electronic, vibrational, and rotational states of a resulting ion, and (c) the multiple ionization that may result from a single electron collision. It is possible to incorporate explicit considerations of all these complications into Eqs. (1.1) and (1.2), as seen in the Appendix of Ref. 8, for instance. Major conclusions of the present paper remain intact under these complications.

II. VARIATIONAL PRINCIPLE FOR THE FOWLER EQUATION

We define the probabilities per inelastic collision

$$p_m(T)\equiv\frac{\sigma_m(T)}{\sigma_{\mathrm{tot}}(T)},\quad q(T,E)\equiv\frac{d\sigma_i(T,E)/dE}{\sigma_{\mathrm{tot}}(T)}, \tag{2.1}$$

where m stands for i or s, and write Eq. (1.1) as

$$\Omega_T N(T)=p(T), \tag{2.2}$$

where we have dropped the subscripts on $N(T)$ and $p(T)$. The appropriate subscript i or s will give the Fowler equation appropriate to ionization or excitation yield. The symbol Ω_T in Eq. (2.2) denotes a linear difference-integral operator common to all m defined by

$$\Omega_T N(T)\equiv N(T)-\sum_n p_n(T)N(T-E_n)-\int_I^{(T+I)/2}dE'q(T,E')[N(T-E')+N(E'-I)]. \tag{2.3}$$

Note that Ω_T acts on a function $N(T)$ of T and also depends explicitly on T through $p_n(T)$, $q(T,E')$, and the upper limit of the integration.

We now seek a variational principle for the value of N at some specific energy T_0, say $N(T_0)$. Following a general procedure,[17-19] we write as a variational estimate $N_v(T_0)$

$$N_v(T_0)=N_t(T_0)-\int_0^\infty dT\,L_t(T_0,T)[\Omega_T N_t(T)-p(T)], \tag{2.4}$$

where $N_t(T)$ is a known "trial" function, which is our first guess for the solution of Eq. (2.2) and which may contain variational parameters. The function $L_t(T_0,T)$ is a trial function for the so-called Lagrange (multiplier) function $L(T_0,T)$. The upper limit of the integral on the right-hand side of Eq. (2.4) has been put as infinity with the (implicit) stipulation that $L(T_0,T)=0$ for $T_0>T$. We shall use similar procedures in the following development whenever they seem to cause no ambiguity.

Because the general procedure[17-19] for formulating a variational principle may be obscure to our readers, we present an explanation of the meaning of Eq. (2.4). First of all, if one knows the exact solution $N(T)$ of Eq. (2.2), then the integral term in Eq. (2.4) vanishes for any $L_t(T_0,T)$. If one knows only a trial solution $N_t(T)$, then the quantity $\Omega_T N_t(T)-p(T)$ is nonvanishing at various T and will cause errors in $N(T_0)$, i.e., the quantity we want to determine. How these errors at each T affect $N(T_0)$ will depend upon both T and T_0. The function $L_t(T_0,T)$ represents the weight by which the errors at each T affect $N(T_0)$. Among all possible choices of $L_t(T_0,T)$, there is the best we can choose under a criterion, i.e., under the requirement that Eq. (2.4) contains vanishing terms that are first order in $\delta N = N_t - N$ and $\delta L = L_t - L$. The function $L(T_0,T)$ chosen in this way compensates errors in $N_t(T)$ and leads to a variational estimate of $N(T)$. As we shall show, the use of exact $L(T_0,T)$ in Eq. (2.4) gives a so-called variational identity, in which errors in $N_t(T)$ are fully corrected for so that exact $N(T)$ is obtained from any trial $N_t(T)$ if exact $L(T_0,T)$ is given. In this sense, $L(T_0,T)$ plays the role similar to that of the generalized force in classical mechanics. (By the term "variational principle," we mean throughout the present paper an expression that is *stationary* with respect to small variations in unknown functions, rather than an expression that is maximal or minimal. Some of our variational results may indeed be maximal or minimal, but we defer the examination of this issue to future work.)

Adopting an inner-product notation for the integral in Eq. (2.4), and setting terms on the right-hand side of Eq. (2.4) that are linear in the first-order error δN equal to zero, we have

$$\delta N(T_0) - (L(T_0,T),\ \Omega_T \delta N(T)) = 0, \tag{2.5}$$

where the repeated symbol T represents an integration variable.

It is possible to introduce an adjoint operator $\Omega_T^\dagger$ so that the operator in the inner product in Eq. (2.5) can be transferred to act on $L(T_0,T)$; in other words, we define $\Omega_T^\dagger$ by the identity $(L(T_0,T),\ \Omega_T\delta N(T)) = (\Omega_T^\dagger L(T_0,T),\ \delta N(T))$. Then, we obtain the equation for $L(T_0,T)$ in the form

$$\Omega_T^\dagger L(T_0,T) = \delta(T_0 - T). \tag{2.6}$$

This is the requisite equation for the Lagrange function and the variational principle is now formally complete because trial solutions of Eqs. (2.2) and (2.6) on insertion into Eq. (2.4) will yield an $N_v(T_0)$ that differs from the exact $N(T_0)$ only by errors of second and higher order.

We now discuss an explicit construction of the adjoint operator. For this purpose, it is convenient to recast Eq. (2.3) by simple changes of variables in the integrals into a form such that $\Omega_T\delta N(T)$ in Eq. (2.5) involves δN having the same argument in all the terms. Thus, we write

$$\begin{aligned}\Omega_T\delta N(T) = \int_I^\infty & dE\ \delta(T-E) \\ & \times\Big(1 - \sum_n p_n(E)\exp(-E_n\overrightarrow{\partial}_E)\Big)\,\delta N(E) \\ & + \int_{T-I}^{(T+I)/2} dE\, q(T,T-E)\,\delta N(E) \\ & - \int_0^{(T-I)/2} dE\, q(T,E+I)\,\delta N(E),\end{aligned} \tag{2.7}$$

where the notation $\exp(-E_n\overrightarrow{\partial}_E)\delta N(E)$ formally represents $\delta N(E - E_n)$, as given by the Taylor expansion. The arrow indicates that the operator $\exp(-E_n\overrightarrow{\partial}_E)$ acts on any operand to the right. With this form, the inner product of Eq. (2.5) involves a double integral $\int_I^\infty dT \int_I^\infty dE$. All that remains is to interchange the integrations so that Eq. (2.5) can be written as

$$\int_I^\infty dE\,[\delta(T_0 - E) - \Omega_E^\dagger L(T_0,E)]\,\delta N(E) = 0, \tag{2.8}$$

where the expression in the square brackets will involve the T integration and explicitly display the structure of the adjoint operation. The interchanging of integrations can be cast in the form of a compact general prescription, fully discussed in Appendix A. Accordingly,

$$\text{if } \Omega \text{ involves } \int_{b_1}^{\alpha(T)} dE, \text{ then } \Omega^\dagger \text{ has } \int_{\alpha^{-1}(E)}^{b_2} dT, \tag{2.9}$$

where b_1 and b_2 are the two boundaries of the range of integration (here I and ∞). That is to say, when one operator involves integrations from one boundary to some function of T, i.e., $\alpha(T)$, then the adjoint operator has its range run from the "inverse" of $E = \alpha(T)$, namely $T = \alpha^{-1}(E)$ to the other boundary. [We assume here that $E = \alpha(T)$ is a monotonic single-valued function of T so that the inverse is defined unambiguously.] Thus, for instance, the last term in Eq. (2.7) goes over into $-\int_{2E+I}^\infty dT\, L(T_0,T)q(T,E+I)$.

With the prescription given by (2.9) and with the exponential operator in Eq. (2.7) taken to act to the left in the adjoint operator, we have

$$\begin{aligned}\Omega_E^\dagger L(T_0,E) = \int_I^\infty & dT\,\delta(T-E)L(T_0,T) \\ & \times[1 - \sum_n p_n(E)\exp(E_n\overleftarrow{\partial}_E)] \\ & + \int_{2E+I}^{E+I} dT\, L(T_0,T)q(T,T-E) \\ & - \int_{2E+I}^\infty dT\, L(T_0,T)q(T,E+I),\end{aligned} \tag{2.10}$$

where the arrow on top of $\overrightarrow{\partial}_E$ denotes that it acts on any operand to the *left*. Thus, Eq. (2.6) can now be written out in full as

$$\begin{aligned}\Omega_T^\dagger L(T_0,T) = & \sum_n p_n(T+E_n)L(T_0,T+E_n) \\ & + \int_{T+I}^{2T+I} dE\, q(E,E-T)L(T_0,E) \\ & + \int_{2T+I}^\infty dE\, q(E,T+I)L(T_0,E) \\ = & \ \delta(T_0 - T).\end{aligned} \tag{2.11}$$

With a trivial change of variables in the first integral on the right-hand side, Eq. (2.11) is seen to be identical to Eq. (1.2). The Lagrange adjoint function is, therefore, the Spencer-Fano y function, apart from a multiplicative factor. From Eqs. (2.11) and (1.2), we can determine the factor and write

$$L(T_0,T)=\mathfrak{N}\sigma_{\text{tot}}(T)y(T_0,T)\,. \qquad (2.12)$$

Since we have been dealing in Eq. (2.2) simultaneously with all the Fowler equations for the different kinds of yields s, we conclude that $y(T_0,T)$ is the universal adjoint function for all the Fowler functions. In fact, Eq. (1.3), for the yields as simple quadrature over $y(T_0,T)$, is now recovered as a trivial identity that follows from Eq. (2.6):

$$\begin{aligned} N(T_0) &\equiv N(T_0)-(\delta(T_0-T)-\Omega_T^\dagger L(T_0,T),\,N(T)) \\ &=(\Omega_T^\dagger L(T_0,T),\,N(T)) \\ &=(L(T_0,T),\,p(T))\,, \end{aligned} \qquad (2.13)$$

where the last equality follows by switching operators inside the inner product and using Eq. (2.2). With L given in Eq. (2.12), Eq. (2.13) is identical to Eq. (1.3).

An alternative form of the variational identity[17] follows by writing

$$\begin{aligned} N(T_0) &\equiv N(T_0)+(\delta(T_0-T)-\Omega_T^\dagger L(T_0,T),\,\delta N(T)) \\ &=N_t(T_0)-(\Omega_T^\dagger L(T_0,T),\,N_t(T)-N(T)) \\ &=N_t(T_0)-(L(T_0,T),\,\Omega_T N_t(T)-p(T))\,. \end{aligned} \qquad (2.14)$$

As usual, replacement of L in the above variational identity by L_t leads[17] to the variational principle in Eq. (2.4).

Had we started with the Spencer-Fano formalism in Eq. (1.2) and sought variational principles, say one for $N(T_0)=(L(T_0,T),p(T))$, we would have written

$$\begin{aligned} N_v(T_0) &= (L(T_0,T),\,p(T))_v=(L_t(T_0,T),\,p(T)) \\ &\quad +(\delta(T_0,T)-\Omega_T^\dagger L_t(T_0,T),\,\Lambda_t(T))\,, \end{aligned} \qquad (2.15)$$

where the defining Eq. (1.2) or, equivalently, Eq. (2.6) is incorporated through a Lagrange function $\Lambda_t(T)$. Its defining equation follows by now setting all δL terms equal to zero, and we find

$$\Omega_T\Lambda(T)=p(T)\,. \qquad (2.16)$$

Thus, we now observe that the Fowler function $N(T)$ is the Lagrange function in this case.

The variational treatment demonstrates, among other things, the complete equivalence and the close connections between the two traditional approaches to the mean yields for a given set of cross-section data—they are adjoints in a very well-defined sense. Many features, some of which are well known and others new, now fall into place. For instance, adjointness always involves,[17-19] as one of its general characteristics, an interchange of the role of boundaries. We have seen this explicitly in Eq. (2.9) and now, in the light of this, it is natural that the Fowler equations are solved conveniently by starting at $T=I$ and ascending, while the Spencer-Fano equation is solved by starting at $T=T_0$ and descending in energy.

In addition, there is a link between the behavior of $N_s(T)$ within a few multiples of the threshold and the behavior of $y(T_0,T)$ for T near T_0 to within a few multiples of I. The degradation spectrum contains structure for T near the source energy T_0. That was discussed by Fano[20] with primary reference to heavy particle slowing down and was demonstrated for electrons[10] by numerical solution of the Spencer-Fano equation. Lewis[21] discussed a related phenomenon: oscillations in the yield curve of nuclear reactions induced by heavy charged particles. This nuclear "Lewis effect" has been observed experimentally.[22]

Miller[7] found the corresponding structure in $N_i(T)$ for helium through numerical solution of the Fowler equation and discussed its origin—the opening of new channels for energy loss. Hence, $N_i(T)$ contains structure near $T=E_1+I$ and $2E_1+I$, where E_1 is the lowest electronic excitation energy (19.8 eV for helium). Structure in N_s was also found and discussed by Jones[23] as well as Cravens, Victor, and Dalgarno.[24] This structure apparently does not emerge in the usual continuous slowing-down approximation. Recent calculations by Douthat[25] on electron degradation in molecular hydrogen indicate the great sensitivity of the low-energy structure in $N_i(T)$ to the choice of cross-section data. Also, recent measurements[26] of the ionization yield in molecular hydrogen indeed show a small slope discontinuity at an expected T value, i.e., $T=E_1+I$.

Application of the variational principle, Eq. (2.4). We discuss here only a simple application, again designed to throw additional light on a known result. Consider the following simple choice for the trial functions in Eq. (2.4):

$$N_{it}(T)=\frac{(T-U)}{W_a}\,, \qquad L_t(T_0,T)=A\delta(T_0-T)+B\,, \qquad (2.17)$$

where U, W_a, A, and B are variational parameters and the form of L_t has been surmised on the basis of the δ-function source term in the defining equation (2.11). Note that $N_{it}(T)$ and $L_t(T_0,T)$ have two parameters each. Generally speaking, any unknown function and its adjoint should contain the same number of linear parameters. This is necessary to obtain a consistent set of algebraic equations for the parameters.

Substituting Eq. (2.17) into Eq. (2.4) and varying the parameters to make $N_v(T_0)$ stationary, we obtain a set of homogeneous equations. We have thence

$$W_a = \sum_n \frac{E_n \sigma_n(T_0)}{\sigma_i(T_0)} + I + U, \tag{2.18}$$

together with a compatibility condition

$$\frac{\int_I^{T_0} dT \left[\sum_n E_n \sigma_n(T) + I\sigma_i(T)\right]}{\int_I^{T_0} dT\, \sigma_i(T)} = \frac{\sum_n E_n \sigma_n(T_0) + I\sigma_i(T_0)}{\sigma_i(T_0)}. \tag{2.19}$$

This result makes contact with the linear dependence of $N_i(T_0)$ at high energies T_0 that was argued for by Inokuti,[8] who showed that this is true if $\sum_n E_n \sigma_n(T)/\sigma_i(T)$ is slowly varying with respect to T [this is equivalent to Eq. (2.19)] and then W_a and U are linked according to Eq. (2.18). The Inokuti argument now takes on some added justification as a variational result.

III. VARIATIONAL PRINCIPLE FOR THE SPENCER-FANO EQUATION

In Eqs. (2.15) and (2.16), we considered the possibility of starting with the L function defined in Eq. (2.6) and seeking a variational principle for its inner product with a known function $p(T)$. We can also seek a variational principle for L itself. There is considerable merit in doing so because we will not only find that such a variational principle is more suitable for numerical handling but also, once a variationally accurate Spencer-Fano function is available, all the yields calculated from it through Eq. (1.3) will also be automatically variational results.

Once again, we begin with the expression

$$L_v(T_0, T) = L_t(T_0, T) + (\delta(T_0 - E) - \Omega_E^\dagger L_t(T_0, E),\ \mathcal{L}_t(E, T)) \tag{3.1}$$

for a variational estimate $L_v(T_0, T)$, with a trial function $\mathcal{L}_t(E, T)$ for its adjoint $\mathcal{L}(E, T)$. We then take the usual step of equating with zero the first-order terms in $\delta L = L - L_t$ and $\delta\mathcal{L} = \mathcal{L} - \mathcal{L}_t$, and obtain

$$(\delta L(T_0, E), \delta(E - T)) - (\Omega_E^\dagger \delta L(T_0, E), \mathcal{L}(E, T)) = 0,$$

from which the defining equation

$$\Omega_E \mathcal{L}(E, T) = \delta(E - T) \tag{3.2}$$

for the new Lagrange function $\mathcal{L}(E, T)$ follows. Though seemingly different, the function $\mathcal{L}$ is identical to L, as can be seen below. Multiplying Eq. (3.2) from the left by $L(T_0, E)$ and forming the inner product, we have

$$(L(T_0, E),\ \Omega_E \mathcal{L}(E, T)) = (L(T_0, E),\ \delta(E - T)).$$

By the definition of the adjoint operator $\Omega_E^\dagger$ and by use of Eq. (2.6), the same quantity can be written as

$$(\Omega_E^\dagger L(T_0, E),\ \mathcal{L}(E, T)) = (\delta(T_0 - T),\ \mathcal{L}(E, T)).$$

Therefore,

$$\mathcal{L}(T_0, T) = L(T_0, T). \tag{3.3}$$

The Spencer-Fano function is an adjoint of itself. This makes the variational principle in Eq. (3.1) particularly suitable for numerical calculations because any linear parameters in the trial function will appear quadratically in the second term in Eq. (3.1), whereas they come in linearly in the first term and, therefore, on making the expression stationary with respect to these parameters, one will always get inhomogeneous equations for them. There are no complications as there were in applying the variational principle in Eq. (2.4) with Eq. (2.17), which led to homogeneous equations with solutions only when the determinant vanished. From the point of view of numerical stability, therefore, a variational principle of the form in Eq. (3.1) is preferred. As a by-product of deriving this principle, we have in Eq. (3.2) an alternative form of the Spencer-Fano equation. Instead of the original form, Eq. (2.6) with an operation of $\Omega^\dagger$ on the second argument, we now have operations by Ω *on the first argument.* Physically speaking, Eq. (3.2) expresses the alternative effects, on the degradation spectrum, of *the next collision* that an electron of energy E undergoes. Equation (3.2) is certainly correct, but is impractical from a point of view other than the variational principle; the direct solution of Eq. (3.2) must start from $E = E_1$ and ascend in E, but one does not know the solution at $E = E_1$ in advance. By the same token, it is perfectly correct to write the Fowler equation (2.2) in the form

$$\Omega_T^\dagger N(T) = p(T), \tag{3.4}$$

but the direct solution must start at high T values, for which one generally does not know the solution. Thus we now see that Ω_T and $\Omega_T^\dagger$ are two alternative modes of description of the same physical effect and that one may use either of the two modes to formulate the mathematics. This connection is similar to adjoint functions in transport theories for γ rays[13] and for neutrons.[14-16]

IV. STATISTICAL FLUCTUATIONS IN THE YIELD AND THE FANO FACTOR

The precise history of individual electrons degrading in a medium is stochastic, and so is the yield of any initial species. If one repeatedly measures the number of ions, for example, created by the complete slowing down of a single electron of initial kinetic energy T in the same medium, measured values will show a statistical distribution. It is the *mean* of this distribution that is given as the solution $N_i(T)$ of the Fowler equation. The distribution and its characteristics such as the variance are important in radiation physics and dosimetry.

A. Ionization yield

Let $P(T,j)$ be the probability that an electron of energy T produces *exactly* j ion pairs upon complete degradation, and consider the simplest medium consisting of molecules having a single ionization threshold I and characterized by the probabilities $p_n(T)$, $p_i(T)$, and $q(T,E)dE$ as in Sec. I. Then, $P(T,j)$ obeys the difference-integral equation[27]

$$P(T,j)=\sum_n p_n(T)P(T-E_n,j)+\sum_{k=0}^{j-1}\int_I^{(T+I)/2} dE\, q(T,E)P(T-E,k)\times P(E-I,j-k-1)\,, \tag{4.1}$$

where the second integral term is zero for $j=0$. Each term on the right-hand side represents alternative contributions to $P(T,j)$ depending upon the nature of an inelastic collision that an electron of energy T undergoes. If that collision results in the excitation n, there will be an electron of energy $T-E_n$, which will contribute $P(T-E_n,j)$ to $P(T,j)$. The probability of this event is $p_n(T)$. Summing the combined contributions $p_n(T)P(T-E_n)$ over all n, one obtains the first term. If that collision results in ionization, there will be an electron of energy $T-E$ and another with energy $E-I$; each of these electrons will generate various numbers of further ion pairs. The combined contributions of that ionizing collision and its subsequent ionizations are given by the second term on the right-hand side; the sum over k and the integral over E represent all the possible alternatives.

The function $P(T,j)$ not only obeys Eq. (4.1) but also is subject to the boundary condition that

$$P(T,j)=\delta_{j0} \quad \text{for } T<I\,, \tag{4.2}$$

which means that no ions can be generated by an electron of kinetic energy less than I.

It is possible to formulate a variational principle for $P(T,j)$ itself, as we indeed do in Sec. V. However, we consider here the moment

$$M(T,\mu)=\sum_{j=0}^{\infty} j^{\mu}P(T,j) \tag{4.3}$$

of μth order, where $\mu=0,1,2,\ldots.$ Multiplying Eq. (4.1) with j^{μ} and summing over j, one obtains

$$M(T,\mu)=\sum_n p_n(T)M(T-E_n,\mu)+\int_I^{(T+I)/2} dE\, q(T,E)\sum_{j=1}^{\infty}\sum_{k=0}^{j-1} j^{\mu}P(T-E,k)P(E-I,j-k-1)\,. \tag{4.4}$$

The double summation under the integral can be rewritten as $\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}$ by use of the index $l=j-k-1$. Thus, the double sum is expressed as

$$\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}(k+l+1)^{\mu}P(T-E,k)P(E-I,l)=\sum_{l=0}^{\infty}\sum_{k=0}^{\infty}\sum_{\nu=0}^{\mu}\sum_{\nu'=0}^{\nu}\binom{\mu}{\nu}\binom{\nu}{\nu'}k^{\nu-\nu'}l^{\nu'}P(T-E,k)P(E-I,l)\,,$$

where $\binom{\mu}{\nu}$ and $\binom{\nu}{\nu'}$ are binomial coefficients. Consequently, one obtains the equation

$$M(T,\mu)=\sum_n p_n(T)M(T-E_n,\mu)+\sum_{\nu=0}^{\mu}\sum_{\nu'=0}^{\nu}\binom{\mu}{\nu}\binom{\nu}{\nu'}\int_I^{(T+I)/2} dE\, q(T,E)M(T-E,\nu-\nu')\,M(E-I,\nu') \tag{4.5}$$

for any moment. According to Eq. (4.2), $M(T,\mu)$ obeys the boundary condition that

$$M(T,\mu)=\delta_{\mu 0} \quad \text{for } T<I\,. \tag{4.6}$$

Thus, the problem of finding $M(T,\mu)$ is now completely defined.

For $\mu=0$ in particular, one has

$$M(T,0)=\sum_n p_n(T)M(T-E_n,0)+\int_I^{(T+I)/2} dE\, q(T,E)M(T-E,0)\times M(E-I,0)\,, \tag{4.7}$$

and

$$M(T,0)=1 \ \text{ for } T<I. \tag{4.8}$$

One can solve Eq. (4.7) by ascending in T. In the initial interval $I<T<I+E_1$ (where E_1 is the lowest excitation threshold energy), for example, one has

$$\begin{aligned} M(T,0)={}&p_1(T)M(T-E_1,0)\\ &+\int_I^{(T+I)/2} dE\, q(T,E)M(T-E,0)\\ &\times M(E-I,0). \end{aligned} \tag{4.9}$$

One may equate all the M's on the right-hand side with unity because of Eq. (4.8) and therefore obtain

$$M(T,0)=p_1(T)+p_i(T)=1 \tag{4.10}$$

for $I<T<I+E_1$. It is straightforward to extend this process to show that

$$M(T,0)=1 \ \text{ for any } T. \tag{4.11}$$

Equation (4.11) represents the conservation of the total probability. Thus, we have seen that Eq. (4.1) is indeed compatible with this basic requirement.

Now it is convenient to recast Eq. (4.5) in a slightly different form by separating two terms containing the μth moment in the double summation, i.e., the terms with $\nu=\mu$, $\nu'=0$ and with $\nu=\mu$, $\nu'=\mu$, and at the same time by using Eq. (4.11). Namely, we write

$$\begin{aligned} M(T,\mu)={}&\sum_n p_n(T)M(T-E_n,\mu)+\int_I^{(T+I)/2} dE\, q(T,E)\left[M(T-E,\mu)+M(E-I,\mu)\right]\\ &+\sum_\nu{}'\sum_{\nu'}{}'\binom{\mu}{\nu'}\binom{\nu}{\nu'}\int_I^{(T+I)/2} dE\, q(T,E)M(T-E,\nu-\nu')M(E-I,\nu'). \end{aligned} \tag{4.12}$$

where the symbol $\sum_\nu'\sum_{\nu'}'$ denotes the remainder of the sum after excluding those two terms. By definition, the remainder contains *only those moments having order smaller than* μ. It is important to observe that the analytical structure of Eq. (4.12) is in essence identical to that of the Fowler equation. Thus, by use of the same operator Ω_T defined by Eq. (2.3), one can simply rewrite Eq. (4.12) as

$$\Omega_T M(T,\mu)=R(T,\mu), \tag{4.13}$$

where the inhomogeneous term $R(T,\mu)$ is given by

$$\begin{aligned} R(T,\mu)={}&\sum_\nu{}'\sum_{\nu'}{}'\binom{\mu}{\nu}\binom{\nu}{\nu'}\\ &\times\int_I^{(T+I)/2} dE\, q(T,E)\\ &\times M(T-E,\nu-\nu')\,M(E-I,\nu'). \end{aligned} \tag{4.14}$$

For instance, consider $M(T,1)$. The inhomogeneous term reduces to

$$\begin{aligned} R(T,1)&=\int_I^{(T+I)/2} dE\, q(T,E)M(T-E,0)M(E-I,0)\\ &=p_i(T) \end{aligned} \tag{4.15}$$

by use of Eqs. (2.1) and (4.11), and Eq. (4.13) reduces to the Fowler equation (1.1) itself. Further, the boundary condition [Eq. (4.6)] for $M(T,1)$ is the same as that for $N_i(T)$. Therefore, $M(T,1)$ is nothing but $N_i(T)$, as it should be.[27]

Suppose that we already know $M(T,1)$, and let us consider Eq. (4.13) for $M(T,2)$. The inhomogeneous term $R(T,2)$ is completely calculable from $M(T,1)$ and the cross-section data, and is thus a known function. It is in principle straightforward to solve Eq. (4.13) for $M(T,2)$ now; indeed any algorithm for solving the Fowler equation immediately applies here. Once $M(T,2)$ is obtained, one can evaluate the inhomogeneous term $R(T,3)$ and then solve Eq. (4.13) once again for $M(T,3)$. This process of unravelling $M(T,\mu)$ as a sequence in μ may be continued indefinitely. Having thus determined $M(T,\mu)$ for many integers μ, one can in principle derive therefrom $P(T,j)$ by an inverse Mellin transform or by the use of a moment theory.

After the long preamble we now turn to the variational treatment, i.e., the theme of the present paper. It is straightforward to formulate the variational principle for $M(T,\mu)$ for $\mu=2,3,4\ldots$, in the same way as we have seen it in Sec. II. It is evident from Eq. (4.13) that the function adjoint to $M(T,\mu)$ for any μ is nothing but $L(T_0,T)$ of Sec. II, or the product of $\mathfrak{N}\sigma_{\text{tot}}(T)$ with the Spencer-Fano $y(T_0,T)$ function. Through an argument precisely parallel to that developed in Sec. II, one arrives at

$$M(T_0,\mu)=(L(T_0,T),R(T,\mu)), \tag{4.16}$$

a relation which is a generalization of Eq. (2.13). In the inner-product notation, the repeated variable T is the variable of integration, as in Eq. (2.13). Notice, more importantly, that Eq. (4.16), like Eq. (2.13), is an *identity* rather than a variational estimate, although it has emerged from a variational treatment.

To see the significance of Eq. (4.16), let us consider $M(T,2)$, which determines the variance $D(T)$ of the number of ions produced, as defined by

$$D(T)=\sum_{j=0}^{\infty}[j-M(T,1)]^2P(T,j)$$

$$=M(T,2)-[M(T,1)]^2\,, \tag{4.17}$$

a concept which was first introduced by Fano[28] and has been discussed by Knipp *et al.*,[27] Herring and Merzbacher,[29] van Roosbroek,[30] Alkhazov and Vorob'ev,[31] and Alkhazov.[32] In particular, Fano[28] showed that $D(T)$ should be nearly proportional to $N_i(T)$ for $T \gg I$ on general grounds, and wrote in effect

$$D(T)=F(T)N_i(T)\,. \tag{4.18}$$

The factor $F(T)$, customarily called the Fano factor, is of the order of magnitude of unity and approaches a constant value for $T \gg I$.

According to Eq. (4.16), one can readily compute $M(T,2)$ by quadrature from the knowledge of $L(T_0,T)$ and $R(T,1)$. The explicit form of $R(T,2)$ is

$$R(T,2)=2\int_I^{(T+I)/2}dE\,q(T,E)$$

$$\times[M(T-E,1)M(E-I,1)$$

$$+M(T-E,1)+M(E-I,1)]$$

$$+p_i(T)\,, \tag{4.19}$$

according to Eq. (4.14). Now recall Eq. (2.13), which says that $M(T_0,1)=N_i(T_0)$ is the inner product of $p_i(T)$ and $L(T_0,T)$. By combining Eq. (2.13) with Eqs. (4.16) and (4.19), we now see that $M(T,2)$ can be expressed as

$$M(T,2)=(L(T,T_1),\,R(T_1,2))$$

$$=\Big(L(T,T_1),2\int_I^{(T_1+I)/2}dE\,q(T_1,E)\,[(L(T_1-E,T_2),\,p_i(T_2))(L(E-I,T_3),\,p_i(T_3))$$

$$+(L(T_1-E,T_2),\,p_i(T_2))+(L(E-I,T_2),\,p_i(T_2))]+p_i(T_1)\Big)\,, \tag{4.20}$$

where the symbols T_1, T_2, and T_3 repeated within each inner product are integration variables. Thus we now see that $M(T,2)$ may be evaluated by repeated quadratures once $L(T_0,T)$ is known. It is also noteworthy that the expression for $M(T,2)$ contains terms up to the third order in L, while the expression [Eq. (2.13)] for $M(T,1)=N_i(T)$ is linear in L. [In general, a similar expression for $M(T,\mu)$ in terms of L can be derived; it contains terms up to $(2\mu+1)$st order in L.]

Thus, continuing the same line of argument, we arrive at the following conclusion. The knowledge of $L(T_0,T)$ enables one to evaluate not only $M(T,1)=N_i(T)$ and $M(T,2)$ [or thence $D(T)$], but all higher moments $M(T,\mu)$, $\mu \geq 3$ [and thence $P(T,j)$]. In other words, the knowledge of the Spencer-Fano function $y(T_0,T)$ [which is in essence equivalent to $L(T_0,T)$] implies the full knowledge of $P(T,j)$ introduced by Knipp *et al.*[27] The conclusion that the Spencer-Fano function contains all information about statistical fluctuations is new to the best of our knowledge.

Finally, it may be added that the equation for $D(T)$ derived by Knipp *et al.*[27] also has the same analytical structure as the Fowler equation, i.e.,

$$\Omega_T D(T)=r(T)\,, \tag{4.21}$$

where the inhomogeneous term $r(T)$ is different but derivable from $R(T,2)$ of Eq. (4.19); it is expressed as

$$r(T)=\sum_n p_n(T)[N_i(T)-N_i(T-E_n)]^2$$

$$+\int_I^{(T+I)/2}dE\,q(T,E)[N_i(T-E)+N_i(E-I)$$

$$+1-N_i(T)]^2\,. \tag{4.22}$$

The function adjoint to $D(T)$ is again $L(T_0,T)$, and we have

$$D(T)=(L(T_0,T),\,r(T))\,, \tag{4.23}$$

through the same argument as before [cf. Eqs. (2.13) and (4.16)].

Application of the variational principle for $D(T)$. Through an argument similar to that leading to Eq. (2.4), it is straightforward to write down an expression for a variational estimate $D_v(T_0)$ in terms of trial functions $D_t(T)$ and $L_t(T_0,T)$, i.e.,

$$D_v(T_0)=D_t(T_0)-\int_I^{\infty}dT\,L_t(T_0,T)$$

$$\times[\Omega_T D_t(T)-r(T)]\,. \tag{4.24}$$

Our application of this expression closely follows the treatment of $N_i(T)$ in Eqs. (2.17)–(2.19). A choice of the trial functions in Eq. (2.4) may have been

$$N_{it}(T)=T/W,\quad L_i(T_0,T)=A\delta(T_0-T)\,, \tag{4.25}$$

which is simpler than Eq. (2.17). This choice in Eq. (2.4), together with a varying of A and W to make $D_v(T_0)$ stationary, leads to

$$W=\sum_n \frac{E_n\sigma_n(T_0)}{\sigma_i(T_0)}+I\,, \tag{4.26}$$

a simpler version of Eq. (2.18).

A similar choice, with variational parameters C and B,

$$D_i(T)=CT,\quad L_i(T_0,T)=B\delta(T_0-T), \tag{4.27}$$

in Eq. (4.24) and some algebra lead to

$$C=\frac{\sum_n E_n^2\sigma_n(T_0)/\sigma_i(T_0)+(W-I)^2}{W^3}\,, \tag{4.28}$$

where $W=T_0/N_i(T_0)$. From Eq. (4.18), the Fano factor is thereby variationally estimated as

$$F(T_0)=\frac{\sum_n E_n^2\sigma_n(T_0)/\sigma_i(T_0)+(W-I)^2}{W^2}\,. \tag{4.29}$$

This result coincides with Eq. (18) of Ref. 27, i.e., an expression derived earlier by Fano[28] through an ingenious consideration. Note that the Fano factor involves the second energy moment of the excitation cross sections, whereas it is the first moment that enters in W. Often, when working with approximate cross sections, one uses sum rules to ensure the total inelastic-scattering cross section (i.e., the zeroth moment) and the stopping power (i.e., the first moment). Thus it is possible that the zeroth and first moment are described adequately even though the higher ones may be substantially in error. This will lead to a good W value but a poor F value. This conclusion is also pertinent to the general observation from numerical work[32,33] that the Fano factor is sensitive—indeed, far more sensitive than the W value—to cross-section data and to the presence of impurity molecules.[32]

B. Yield of initial species other than ions

So far we have discussed the yield of ions and its statistical fluctuations. We shall now outline how to extend the treatment to the yield of any initial species s, e.g., a particular excited state of interest.

Let $P_s(T,j)$ be the probability that an electron causes j molecules to be excited to state s either directly or through all secondary electrons in the course of complete degradation. Within the same premise as in Sec II, $P_s(T,j)$ obeys an equation

$$\begin{aligned}P_s(T,j)=&\,p_s(T)P_s(T-E_s,j-1)\\&+\sum_{n\neq s}p_n(T)P_s(T-E_n,j)\\&+\sum_{k=0}^{j}\int_I^{(T+I)/2}dE\,q(T,E)P_s(T-E,k)\\&\qquad\times P_s(E-I,j-k)\,.\end{aligned} \tag{4.30}$$

This equation can be derived from considerations similar to those leading to Eq. (4.1). Briefly, each term on the right-hand side represents alternative contributions to $P_s(T,j)$, classified according to the kind of inelastic collisions that an electron of energy T undergoes. Notice several differences from Eq. (4.1). First of all, the term representing the excitation of state s has to be isolated from the summation over n, and the second argument in $P_s(T-E_s,j-1)$ is $j-1$ because the very excitation process contributes unity to the yield of s. Secondly, the summation over k in the last term runs up to j, and the second argument in $P_s(E-I,j-k)$ is $j-k$, because an ionization process, represented by this term, does not contribute to the yield of s. By contrast, the corresponding summation in Eq. (4.1) runs up to $j-1$ and the second argument in $P_s(E-I,j-k-1)$ is $j-k-1$. The function $P_s(T,j)$ is subject to the boundary condition

$$P_s(T,j)=\delta_{j0}\quad\text{for } T<E_s\,, \tag{4.31}$$

where E_s is the threshold energy for state s.

The moment

$$M_s(T,\mu)=\sum_{j=0}^{\infty}j^\mu P_s(T,j) \tag{4.32}$$

satisfies an equation

$$\begin{aligned}M_s(T,\mu)=&\,p_s(T)\sum_{\nu=0}^{\mu}\binom{\mu}{\nu}M_s(T-E_s,\nu)+\sum_{n\neq s}p_n(T)M_s(T-E_n,\mu)\\&+\sum_{\nu=0}^{\mu}\binom{\mu}{\nu}\int_I^{(T+I)/2}dE\,q(T,E)M_s(T-E,\mu-\nu)M_s(E-I,\nu)\,,\end{aligned} \tag{4.33}$$

with the condition

$$M_s(T,\mu)=\delta_{\mu 0} \text{ for } T<E_s. \tag{4.34}$$

It is possible to draw the following conclusions from Eqs. (4.33) and (4.34). First, the conservation of total probability, i.e.,

$$M_s(T,0)=1 \text{ for any } T \tag{4.35}$$

holds. Second, the moment equation can be recast into the standard Fowler form

$$\Omega_T M_s(T,\mu)=R_s(T,\mu), \tag{4.36}$$

where the inhomogeneous term $R_s(T,\mu)$ is given in terms of lower moments by

$$R_s(T,\mu)=p_s(T)+\sum_{\nu=1}^{\mu-1}\binom{\mu}{\nu}\Big[M_s(T-E_s,\nu) + \int_I^{(T+I)/2} dE\, q(T,E)\, M_s(T-E,\mu-\nu) \times M_s(E-I,\nu)\Big]. \tag{4.37}$$

For $\mu=1$ in particular, Eq. (4.36) reduces to the Fowler equation for $N_s(T)$, discussed in Sec. II; in other words, $M_s(T,1)$ is identical to $N_s(T)$. Third, the adjoint of any $M_s(T-E,\mu)$ is the now familiar $L(T_0,T)$. Finally, we have the identity

$$M_s(T_0,\mu)=\big(L(T_0,T),R_s(T,\mu)\big), \tag{4.38}$$

which enables one to calculate by quadrature $M_s(T_0,\mu)$ up to arbitrary high μ, once $L(T_0,T)$ is known.

V. VARIATIONAL TREATMENT OF THE STOCHASTIC YIELD OF IONIZATIONS

In this section we consider the function $P(T,j)$ defined in Eq. (4.1). This probability function embodies the most detailed information possible concerning the ionization yield, within the premise of our discussion. A variational principle for it will, therefore, be the most general result possible for the yield of ions. All other quantities, such as the various moments of the probability function, and the variational principles considered for them in Sec. IV, will follow by taking appropriate moments. Solving for $P(T,j)$ either directly from Eq. (4.1) or through this variational principle or its associated identity, may be more difficult than solving for $N_i(T)$. Construction of the variational principle for Eq. (4.1) remains straightforward, however. In fact, we can anticipate a simplifying aspect. As we saw in Sec. IV, all moments of $P(T,j)$ obey the same Fowler-type equation with the same operator Ω_T so that $L(T_0,T)$ in Eq. (2.11) is the universal adjoint function for *all* the moments. This implies that $L(T_0,T)$ must also be the adjoint function for the stochastic function P itself. This anticipated result is verified below by construction of the variational principle for Eq. (4.1), which initially leads to an apparently more complicated adjoint function. However, a closer examination reveals that it is essentially the degradation spectrum.

The nonlinearity of Eq. (4.1) does not complicate the construction of a variational principle. The clue to this lies in the feature that our general prescription calls for defining the operator through its action on the first-order error (see also, Appendix B).

We can proceed in the construction of a variational principle for $P(T_0,j_0)$ from

$$P_v(T_0,j_0)=P_t(T_0,j_0)-\sum_{j=0}^{\infty}\int_I^{\infty} dT\,\Lambda_t(T_0,j_0,T,j)\Big(P_t(T,j)-\sum_n p_n(T)P_t(T-E_n,j) - \sum_{k=0}^{j-1}\int_I^{\frac{1}{2}(T+I)} dT'\,q(T,T')P_t(T-T',k)P_t(T'-I,j-k-1)\Big), \tag{5.1}$$

where $\Lambda_t(T_0,j_0,T,j)$ is a trial solution of the equation to be obtained for the Lagrange function $\Lambda(T_0,j_0,T,j)$ and $P_t(T,j)\equiv P(T,j)+\delta P(T,j)$, where $P_t(T,j)$ is a trial function for the exact $P(T,j)$. Adopting inner-product notation and summing over repeated indices we have

$$P_v(T_0,j_0)=P_t(T_0,j_0)-\big(\Lambda_t(T_0,j_0,T,j)\;\mathcal{K}_{Tj}[P_t(T,j)]\big), \tag{5.2}$$

where $\mathcal{K}_{Tj}$ is a nonlinear operator defined by

$$\mathcal{K}_{Tj}[P(T,j)]=P(T,j)-\sum_n p_n(T)P(T-E_n) - \sum_{k=0}^{j-1}\int_I^{(T+I)/2} dT'\,q(T,T') \times P(T-T',k)P(T'-I,j-k-1). \tag{5.3}$$

Here we enclose the operand with square brackets to emphasize the nonlinearity of $\mathcal{K}_{Tj}$. We note a difference from the case of linear operators: If Eq. (4.1) were linear, then the variational estimate of Eq. (5.2) would involve only the approximation of replacing Λ by Λ_t and discarding the second-order error $\delta\Lambda\delta P$. In the nonlinear case however, the variational estimate of (5.2) includes additional errors of higher order in δP. These terms of order $(\delta P)^2$ and higher order in δP are present only for nonlinear equations.

In order to identify the equation for $\Lambda(T_0,j_0,T,j)$, we write the identity

$$P(T_0,j_0)=P_t(T_0,j_0) - (\Lambda(T_0,j_0,T,j),\, \mathcal{K}'_{Tj}(P)[\delta P(T,j))]\,, \tag{5.4}$$

where $\mathcal{K}'_{Tj}(P)$ is a new operator that generates the Fréchet derivative,[34] i.e.,

$$\mathcal{K}_{Tj}[P_t(T,j)]=\mathcal{K}_{Tj}[P(T,j)]+\mathcal{K}'_{Tj}(P)[\delta P(T,j)]+\cdots\,. \tag{5.5}$$

The explicit form of (5.5) is obtained by writing (5.3) with P_t in place of P and displaying all terms linear in $\delta P=P_t-P$. A change of the variables of integration and summation so that all terms involve δP with the same argument gives

$$\begin{aligned}\delta P(T,j)-\sum_n p_n(T)\exp(-E_n\vec{\partial}_T)\delta P(T,j)+\sum_{k=0}^{j-1}\int_{T-I}^{(T-I)/2} dT'\,q(T,T-T')\delta P(T',k)P(T-T'-I,j-k-1)\\ -\sum_{k=0}^{j-1}\int_0^{(T-I)/2} dT'\,q(T,T'+I)P(T-T'-I,j-k-1)\delta P(T',k)\,. \end{aligned}\tag{5.6}$$

Writing the first two terms as

$$\sum_{k=0}^{\infty}\delta_{jk}\int_0^{\infty} dT'\,\delta(T-T')\Big(1-\sum_n p_n(T')\exp(-E_n\vec{\partial}_{T'})\Big)\delta P(T',k)$$

permits identification of $\mathcal{K}'_{Tj}(P)[\delta P(T,j)]$. Applying the rules for adjointness given in Eq. (2.9), we can construct $\mathcal{K}'^{\dagger}_{Tj}\Lambda(T_0,j_0,T,j)$, which is

$$\begin{aligned}\Lambda(T_0,j_0,T,j)-\sum_n \Lambda(T_0,j_0,T,j)p_n(T)\exp(E_n\overleftarrow{\partial}_T)+\sum_{m=j+1}^{\infty}\int_{2T+I}^{T+I} dE\,\Lambda(T_0,j_0,E,m)q(E,E-T)P(E-T-I,m-j-1)\\ -\sum_{m=j+1}^{\infty}\int_{2T+I}^{\infty} dE\,\Lambda(T_0,j_0,E,m)q(E,T+I)P(E-T-I,m-j-1)\,. \end{aligned}\tag{5.7}$$

The adjoint equation is thus

$$\mathcal{K}'^{\dagger}_{Tj}\Lambda(T_0,j_0,T,j)=\delta(T_0-T)\delta_{jj_0}\,, \tag{5.8}$$

and the variational principle is now complete.

Equations (5.7) and (5.8) illustrate a general feature (see Appendix B) of the adjoint function, namely, that Λ enters only linearly in the defining equations even for nonlinear problems. Another feature illustrated by Eqs. (5.7) and (5.8) is that the original function P is itself involved in the equation for Λ. This does not detract from the utility of the adjoint function since the variational principle requires only a trial approximation Λ_t to the exact Λ and only a trial P_t is required to obtain Λ_t. (A note of caution is necessary here since in some instances it may be inconsistent to replace P by P_t in the adjoint equation. Such difficulties and their resolution are considered in detail in Ref. 19.)

For the problem of this paper a further simplification occurs since closer examination reveals that P drops out of Eq. (5.8) and Λ is essentially the L function of earlier sections. We note first that the solution of Eq. (5.8) obtains by proceeding stepwise from large values of the second index j and in this domain (i.e., $j>T/I$), $P(T,j)=0$ by conservation of energy. Consequently $\Lambda(T_0,j_0,T,j)$ is not defined for sufficiently large j and can be chosen to be independent of j for $j\geq j_0$. Exercising this option in the choice of $\Lambda(T_0,j_0,T,j)$, we can interchange the order of integration and summation in Eq. (5.7). Since $\sum_{j=k+1}^{\infty}P(E-T,j-k-1)=1$, the summations in Eq. (5.7) collapse leaving the equation with the same form as Eq. (3.2) for $L(T_0,T)$. The index j_0 is a dummy index since it appears in the same way in every term. Hence the identification of Λ with L is justified.

An alternative and perhaps simpler argument proceeds by observing that construction of the variational principle for $P(T_0,j_0)$ is possible without the summation over j of Eq. (5.1), viz., the Lagrange function Λ is common to all j_0 and j. This circumstance arises from the structure of Eq. (4.1) for $P(T,j)$. Since the right-hand side of Eq. (4.1) contains only indices not greater than j, the equation can be viewed as a recursion relation which is linear in the sense that the values of the unknown $P(T,j)$ occur only linearly.

Since the adjoint $\Lambda(T_0, j_0, T, j)$ of $P(T_0, j_0)$ is essentially identical to $L(T_0, T)$ in that both j_0 and j are dummy indices, the results of this section again emphasize that $L(T_0, T)$ is the fundamental quantity in the entire problem. In fact, the results of Sec. IV can also be obtained by considering a variational principle for the moments of $P(T, j)$.

VI. INFLUENCE OF CHANGES IN THE CROSS-SECTION DATA UPON ELECTRON-DEGRADATION QUANTITIES

Our knowledge of the cross-section data is always imperfect, but is being improved from year to year by new experiment and theory. Whenever new information on cross sections reaches us, we want to find out how the prediction of the initial-species yields and of the degradation spectra will be modified in the light of the new information, hopefully without repeating the entire degradation calculation again using a new set of cross-section data.

Furthermore, the medium in which electrons degrade may contain chemical impurities, either intentionally or inadvertently. We want to find out how the chemical impurities affect the yields and the degradation spectra. The presence of chemical impurities causes additional collision processes of electrons, and may be regarded as changes in the cross-section data.

Let us formulate a general theory for answering the questions raised above, provided the changes in the cross-section data are sufficiently small. That is to say, we shall develop a perturbation theory in the language of neutron-reactor physics.[16] Suppose that we have already solved the problem defined by the set of probabilities $\{p_n^{(0)}(T), p_i^{(0)}(T), q^{(0)}(T, E)\}$. The corresponding Fowler operator $\Omega_T^{(0)}$ is given by the same equation as Eq. (2.3) with all the probabilities now having superscript (0). The adjoint operator $\Omega_T^{(0)\dagger}$ is given in the same form as in Eq. (2.10).
Thus, the solutions of the unperturbed problem

$$\Omega_T^{(0)} N_s^{(0)}(T) = p_s^{(0)}(T) , \tag{6.1}$$

$$\Omega_T^{(0)\dagger} L^{(0)}(T_0, T) = \delta(T - T_0) , \tag{6.2}$$

are supposed to be known. Suppose that changes in the cross-section data lead to a new set of collision probabilities

$$p_n(T) = p_n^{(0)}(T) + \epsilon p_n^{(1)}(T) , \tag{6.3}$$

$$p_i(T) = p_i^{(0)}(T) + \epsilon p_i^{(1)}(T) , \tag{6.4}$$

$$q(T, E) = q^{(0)}(T, E) + \epsilon q^{(1)}(T, E) , \tag{6.5}$$

and thence to new operators

$$\Omega_T = \Omega_T^{(0)} + \epsilon \omega_T , \tag{6.6}$$

$$\Omega_T^\dagger = \Omega_T^{(0)\dagger} + \epsilon \omega_T^\dagger , \tag{6.7}$$

where ϵ is a real number introduced for convenience. We shall assume that $\epsilon\omega_T$ and $\epsilon\omega_T^\dagger$ are small compared to $\Omega_T^{(0)}$ and $\Omega_T^{(0)\dagger}$. However, it is convenient to say that we regard ϵ as small compared to unity and the solutions $N_s(T)$ and $L(T_0, T)$ as analytic functions of ϵ in a domain near $\epsilon = 0$. So long as ω_T and $\omega_T^\dagger$ themselves are small, we may put $\epsilon = 1$ in our final result.

Parenthetically we note that the multiplication of all the cross-section data by a scale factor leaves all the probabilities and thence Ω_T and $\Omega_T^\dagger$ invariant. In other words, the electron degradation problem is *linear* so long as it is described by Ω_T and $\Omega_T^\dagger$. [The nonlinearity of Eqs. (4.1) and (4.30) is only superficial, as we saw in Sec. V.] Physically speaking, the degradation problem is linear if the density of electrons present in the medium is negligible compared to the density $\mathfrak{N}$ of molecules, so that one need not consider collisions between two electrons or between an electron and an initial species. When the medium is a plasma, then these collisions are non-negligible and the degradation problem becomes nonlinear. Furthermore, electron collisions with another electron or any ion are governed by Coulomb forces and are therefore highly efficient for the electron slowing down. Indeed, Cravens *et al.*[24] found a strong sensitivity of the ionization yield upon the original electron density, even when it was of the order 10^{-3} $\mathfrak{N}$ or smaller.

Let us return to our theme and consider solving

$$\Omega_T N_s(T) = p_s(T) , \tag{6.8}$$

where Ω_T is given by Eq. (6.6) and $p_s(T)$ by Eq. (6.3) and (6.4). The problem is formally the same as in the beginning of Sec. IV. We may write the same expression as Eq. (2.4), and use $N_s^{(0)}(T_0)$ and $L^{(0)}(T_0, T)$ as trial functions. Then, we have

$$N_v(T_0) = N_s^{(0)}(T_0) - (L^{(0)}(T_0, T),\ \Omega_T N_s^{(0)}(T) - p_s(T)) . \tag{6.9}$$

Next, we use Eqs. (6.1), (6.3), and (6.6) in the right-hand side, and obtain

$$N_v(T_0) = N_s^{(0)}(T_0) - \epsilon (L^{(0)}(T_0, T),\ \omega_T N_s^{(0)}(T) - p_s^{(1)}(T)) . \tag{6.10}$$

This is the solution of the new problem correct to the first order in ϵ. In other words, the inner-product term is the first-order correction to the mean yield resulting from changed cross sections. We may also interpret the quantity $p_s^{(1)}(T) - \omega_T N_s^{(0)}(T)$ as *an effective probability* for the additional production of species s by an electron of energy T. When one evaluates this additional production by the use of exact $L(T_0, T)$, then the probability is certainly $p_s^{(1)}(T)$ itself. When one evaluates it by the use of $L^{(0)}(T_0, T)$, then one should use the effective probability, modified by the term $-\omega_T N_s^{(0)}(T)$, which represents the reduction due to competition with all the other processes.

Furthermore, we may use the right-hand side of Eq. (6.1) as a new trial function for $N_s(T_0)$, and again write down the same expression as Eq. (2.4). Then, we obtain an estimate of $N_s(T_0)$ correct to the order ϵ^2. In principle, we can repeat this process to any order in ϵ and obtain better and better estimates. A similar treatment of $L(T_0, T)$ is also possible. This procedure is an example of supervariational principles in the language of Ref. 19.

Alternatively, we shall derive the same result by the use of a perturbation series. Let us rewrite Eq. (6.8) in the form

$$(\Omega_T^{(0)} + \epsilon\omega_T) N_s(T) = p_s^{(0)}(T) + \epsilon p_s^{(1)}(T), \qquad (6.11)$$

and set

$$N_s(T) = \sum_{\alpha=0}^{\infty} \epsilon^\alpha N_s^{(\alpha)}(T), \qquad (6.12)$$

where $N_s^{(\alpha)}(T)$ for $\alpha \geq 1$ are functions to be determined. Inserting Eq. (6.12) into Eq. (6.11) and comparing each term in the same power in ϵ, we obtain

$$\Omega_T^{(0)} N_s^{(1)}(T) = p_s^{(1)}(T) - \omega_T N_s^{(0)}(T), \qquad (6.13)$$

and

$$\Omega_T^{(0)} N_s^{(\alpha)}(T) = -\omega_T N_s^{(\alpha-1)}(T) \qquad (6.14)$$

for $\alpha \geq 2$.

In Eqs. (6.13) and (6.14) it is the same Fowler operator $\Omega_T^{(0)}$ (for the unperturbed problem) that acts on the unknown function at each step of solution successive in α. As we saw in Sec. II and IV, we can immediately express the solution by the use of the adjoint function $L^{(0)}(T_0, T)$. The result is

$$N_s^{(1)}(T_0) = (L^{(0)}(T_0, T), p_s^{(1)}(T) - \omega_T N_s^{(0)}(T)), \qquad (6.15)$$

and

$$N_s^{(\alpha)}(T_0) = -(L^{(0)}(T_0, T), \omega_T N^{(\alpha-1)}(T)) \qquad (6.16)$$

for $\alpha \geq 2$. In other words, we can calculate $N_s^{(\alpha)}(T_0)$ to any α, by taking an inner product with $L^{(0)}(T_0, T)$. The logical content of Eq. (6.15) is identical to our earlier variational result, i.e., Eq. (6.10); $N_s^{(0)}(T_0) + \epsilon N_s^{(1)}(T_0)$ is the same as the right-hand side of Eq. (6.10).

The analytical structure of $N_s^{(\alpha)}(T_0)$ is easily recognizable. Combining Eqs. (6.15) and (6.16), one may write, for instance,

$$\begin{aligned} N_s^{(2)}(T_0) &= -(L^{(0)}(T_0, T), \omega_T N_s^{(1)}(T)) \\ &= -(L^{(0)}(T_0, T), \omega_T (L^{(0)}(T, T'), p_s(T') \\ &\qquad - \omega_{T'} N_s^{(0)}(T'))). \end{aligned} \qquad (6.17)$$

Symbolically, we may express this result as

$$N_s^{(2)} = -(L^{(0)}, \omega L^{(0)}, p_s - \omega N_s^{(0)}). \qquad (6.18)$$

Generally, we may write in this notation

$$N_s^{(\alpha)} = (-1)^{\alpha-1}(L^{(0)}, \omega L^{(0)}, \omega L^{(0)}, \ldots, p_s - \omega N_s^{(0)}), \qquad (6.19)$$

where $\omega L^{(0)}$ appears $\alpha - 1$ times in succession. Thus the solution of Eq. (6.11) is now complete. It is also straightforward to extend the analysis to $M(T, \mu)$ of Sec. IV. Results are completely analogous.

Finally, we present an analogous treatment of $L(T_0, T)$, i.e., the solution of

$$(\Omega_T^{(0)\dagger} + \epsilon\omega_T^\dagger) L(T_0, T) = \delta(T - T_0). \qquad (6.20)$$

We set

$$L(T_0, T) = \sum_{\alpha=0}^{\infty} \epsilon^\alpha L^{(\alpha)}(T_0, T) \qquad (6.21)$$

in Eq. (6.20) and consider each term in the same power in ϵ. Then we have

$$\Omega_T^{(0)\dagger} L^{(\alpha)}(T_0, T) = -\omega_T^\dagger L^{(\alpha-1)}(T_0, T) \qquad (6.22)$$

for $\alpha \geq 1$.

We now write T' in place of T in this equation and take inner products of both sides with $L^{(0)}(T', T)$.

$$\begin{aligned} &(\Omega_{T'}^{(0)\dagger} L^{(\alpha)}(T_0, T'), L^{(0)}(T', T)) \\ &\qquad = -(\omega_{T'}^\dagger L^{(\alpha-1)}(T_0, T'), L^{(0)}(T', T)). \end{aligned} \qquad (6.23)$$

The left-hand side is $L^{(\alpha)}(T_0, T)$, as the following shows.

$$\begin{aligned} &(\Omega_{T'}^{(0)\dagger} L^{(\alpha)}(T_0, T'), L^{(0)}(T', T)) \\ &\qquad = (L^{(\alpha)}(T_0, T'), \Omega_{T'}^{(0)} L^{(0)}(T', T)) \\ &\qquad = (L^{(\alpha)}(T_0, T'), \delta(T' - T)) = L^{(\alpha)}(T_0, T). \end{aligned}$$

Here use has been made of the adjointness property and of Eqs. (3.2) and (3.3). Consequently, we have

$$\begin{aligned} L^{(\alpha)}(T_0, T) &= -(\omega_{T'}^\dagger L^{(\alpha-1)}, (T_0, T'), L^{(0)}(T', T)) \\ &= -(L^{(\alpha-1)}(T_0, T'), \omega_{T'} L^{(0)}(T', T)). \end{aligned} \qquad (6.24)$$

This enables us to write $L^{(\alpha)}(T_0, T)$ successively, all in terms of $L^{(0)}(T_0, T)$.

First, we have

$$L^{(1)}(T_0,T) = -(L^{(0)}(T_0,T'),\ \omega_{T'}L^{(0)}(T',T)). \tag{6.25}$$

Next, we have

$$L^{(2)}(T_0,T) = ((L^{(0)}(T_0,T'),\ \omega_{T'}L^{(0)}(T',T'')),\ \omega_{T''}L^{(0)}(T'',T)). \tag{6.26}$$

Symbolically, we may express this result as

$$L^{(1)} = -(L^{(0)}, \omega L^{(0)}),$$
$$L^{(2)} = (L^{(0)}, \omega L^{(0)}, \omega L^{(0)});$$

and hence generally as

$$L^{(\alpha)} = (-1)^{\alpha}(L^{(0)}, \omega L^{(0)}, \ldots, \omega L^{(0)}), \tag{6.27}$$

where $\omega L^{(0)}$ appears α times in succession. Alternatively, $L^{(\alpha)}$ may be expressed in terms of repeated $\omega^{\dagger}$, e.g.,

$$L^{(1)} = -(\omega^{\dagger}L^{(0)}, L^{(0)}),$$
$$L^{(2)} = (\omega^{\dagger}\omega^{\dagger}L^{(0)}, L^{(0)}, L^{(0)}),$$

and hence

$$L^{(\alpha)} = (-1)^{\alpha}(\omega^{\dagger}\circ\cdots\omega^{\dagger}L^{(0)}, \ldots, L^{(0)}), \tag{6.28}$$

where $\omega^{\dagger}$ appears α times and $L^{(0)}$ $(\alpha+1)$ times.

In summary, the knowledge of the Spencer-Fano degradation spectrum enables one to calculate any yield and other quantities related to electron degradation in the new problem with modified cross-section data.

VII. CONCLUDING REMARKS

Throughout the present discussion, we have tried to elucidate conceptual relations among different formulations and among different aspects of the electron-degradation problem. We hope that our discussion will help strengthen the understanding of the rich mathematical physics involved in the problem, i.e., a part of what Weinberg and Wigner[35] call the scholarly tradition in neutron-reactor physics. The tool of our treatment was the general variational method,[17-19] and the key notion was the adjoint operator. In fact, the adjoint operator has been used in neutron-reactor physics for a long time, and its power has been demonstrated also for treating *spatial aspects* of the particle-degradation problem.[14-16,35] In consideration of radiation actions on matter in condensed phases, one often finds it important to discuss the spatial distribution of degrading electrons and of initial molecular species; this aspect is commonly referred to as track-structure effects. The notion of the adjoint operator should play a key role in the analysis of the track-structure effects. We hope to explore this surmise in the near future.

It may be useful to comment on different points of emphasis in our problem and in neutron physics. We have discussed in detail fluctuations in the number of initial species (Secs. IV and V). These fluctuations are important in semiconductor detectors and other real situations in which one deals with a small number of initial yields. It seems that an equivalent of the fluctuation problem for neutrons is seldom discussed in reactor physics but may be important in neutron dosimetry.

We have pointed out that the degradation spectrum $y(T_0,T)$ plays the role of a Green's function. However, there is a contrast between $y(T_0,T)$ on the one hand, and the Green's function that appears in quantum mechanics, classical potential theory, and other topics on the other hand. The Green's function in those standard topics usually has a singularity in the domain of a variable of physical interest, for example, the energy in quantum mechanics and the position in classical potential theory. By contrast, $y(T_0,T)$ is smooth in T and T_0, except for structure near $T=T_0$ (the Lewis effect), and it is therefore straightforward to compute integrals (or inner products) involving $y(T_0,T)$. In this sense, $y(T_0,T)$ is similar to the Green's function for the diffusion problem. This similarity is no surprise when we recall that the diffusion process is fundamentally the degradation of particle energy by random collisions.

Finally, the electron degradation in a plasma, i.e., a medium containing charged particles, is a nonlinear problem, as we pointed out in Sec. VI. The use of the adjoint operator in this problem awaits future study.

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APPENDIX A: INTERCHANGE OF MULTIPLE INTEGRATIONS

A crucial step in constructing the adjoint $\Omega^{\dagger}$ of an operator Ω involves transferring the operation of Ω on δN in an inner product

$$(L(T),\, \Omega\,\delta N(T)) \tag{A1}$$

to an operation of $\Omega^\dagger$ on L. When Ω is a differential operator, this requires integration by parts, and, finally (A1) can be cast in the form

$$(\Omega^\dagger L(T),\, \delta N(T)) + \text{boundary terms}. \tag{A2}$$

When Ω is an integral operator, by contrast, the required manipulation is interchanging the order of repeated integrations in (A1). A typical term in (A1) has the structure

$$\int_{b_1}^{b_2} dT \int_{b_1}^{\alpha(T)} dE\, I(T,E)\,\delta N(E), \tag{A3}$$

where b_1 and b_2 are the two boundaries on the range of variables, and $\alpha(T)$ is assumed to be a single-valued function of T. Our aim is to recast (A3) so that the integration over E runs from b_1 to b_2; the rest of the integrand that multiplies $\delta N(E)$ can then be identified with $\Omega^\dagger L(E)$. The switching of the integrations is straightforward if $\alpha(T)$ satisfies

$$\alpha(b_1) = b_1, \quad \alpha(b_2) = b_2. \tag{A4}$$

In that case, as shown in Fig. 1(a) by the solid vertical arrow with the attached horizontal wavy arrow, the integrations in (A3) can be described in the following terms: at a fixed T, the E values run from b_1 up to $\alpha(T)$ along the solid arrow; this solid arrow itself slides from left to right along the wavy arrow from $T = b_1$ to $T = b_2$, sweeping out the diagonally shaded area of integration. The same region of integration can be described, on the other hand, by the other set of arrows shown, where the solid arrow runs, at fixed E, from the $\alpha(T)$ curve to the boundary $T = b_2$ and slides vertically up from $E = b_1$ to $E = b_2$. Thus, (A3) is rewritten as

$$\int_{b_1}^{b_2} dE \int_{\alpha^{-1}(E)}^{b_2} dT\, I(T,E)\,\delta N(E), \tag{A5}$$

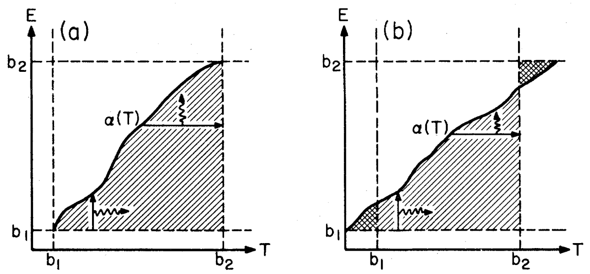

FIG. 1. The domain of repeated integrations in Eq. (A3). (a) Shows the case in which the interchanging of the integrations is straightforward. (b) Shows the case in which extra-boundary terms (represented by the cross-hatched areas) arise.

where $\alpha^{-1}(E)$ represents the value of T at some fixed E such that $\alpha(T) = E$.

In a more general situation, where $\alpha(T)$ does not satisfy Eq. (A4), the following complication can arise. Figure 1(b) shows that, whereas (A3) covers the diagonally shaded area, (A5) covers, in addition, the cross-hatched areas. Then, (A3) cannot be replaced by (A5) without also introducing these "extra-boundary" terms, which are the analog now of the terms in (A2) that are more familiar to us for differential operators. In the problem treated in Sec. II, these extra terms vanish by virtue of the structure of the integrand. Consider, for instance, a representative term in Eq. (2.5) when Eq. (2.7) is substituted into it,

$$\int_I^\infty dT\, L(T_0,T) \int_0^{(T-I)/2} dE\, q(T, E+I)\,\delta N(E). \tag{A6}$$

First, the lower limit on the first integral can be extended down to 0, the cross section q being zero for $T < I$. The upper limit is effectively terminated at T_0 by virtue of the L function existing only in a region where $T \leqslant T_0$. The above expression has, therefore, $b_1 = 0$ and $b_2 = T_0$. No contributions from regions such as the cross-hatched ones in Fig. 1(b) can arise because L and q ensure that the integrand vanishes for $T < b_1$ and $T > b_2$. As a result, (A6) can, in fact, be replaced by

$$\int_I^\infty dE \int_0^{2E+I} dT\, L(T_0,T)\, q(T, E+I)\,\delta N(E). \tag{A7}$$

In all the applications in the present paper, the general prescription of replacing (A3) by (A5) is valid and it is this prescription that has been capsuled in Eq. (2.9).

A remark is also in order regarding difference terms such as the one involving $\exp(-E_n \overrightarrow{\partial}_E)$ in Eq. (2.7). In forming the adjoint operator, which involves switching it to act on the L on the left, similar manipulations for changing the variables of integration are necessary, with an attendant change in the limits of integration. Once again, in general, this can introduce "extra-boundary" contributions. But for the applications in the present paper, where $L(T_0, T)$ is taken to be zero for $T < E_1$, such complications are absent, and the formal replacement of operators acting to the right by making them act on the left constitutes the passage from Ω to $\Omega^\dagger$. Throughout the present paper, trial functions $L_t(T_0, T)$ are always meant to be defined only in the physical region, $E_1 \leqslant T \leqslant T_0$.

APPENDIX B: A NOTE ON NONLINEAR OPERATORS

The construction of variational principles for a function $f(x)$ that obeys a nonlinear equation

$$\Xi_x[f(x)] = 0 \tag{B1}$$

requires first the identification of the operator whose adjoint one wishes to construct. The procedure of our general formalism points the way since we begin by writing

$$f_v(x) = f_t(x) - (\mathcal{L}_t(x,x'), \Xi_{x'}[f_t(x')]), \tag{B2}$$

with the precaution that $\mathcal{L}_t$ of this appendix is not to be confused with the specific $\mathcal{L}$ of Sec. III. With $f_t \equiv f + \delta f$, we then ensure that all terms linear in δf vanish. Since

$$\Xi_{x'}[f_t(x')] = \Xi_{x'}[f(x')] + (\delta\Xi[f]/\delta f)(f_t - f) + \cdots, \tag{B3}$$

the operator involved is the Fréchet (functional) derivative $\Xi'[f]$. When Eq. (B1) is linear in f, Ξ' is independent of f. For nonlinear equations, however, Ξ' itself involves f. As the problem of Sec. V and the following examples illustrate, this in no way complicates the construction of the adjoint equation, which is

$$\Xi_{x'}'^{\dagger}[f]\,\mathcal{L}(x,x') = \delta(x - x'). \tag{B4}$$

Since $\mathcal{L}$ is introduced linearly in Eq. (B2), the adjoint equation always involves $\mathcal{L}$ linearly and although the equation for $\mathcal{L}$ now involves f, this does not necessarily detract from its utility in that a formal solution for $\mathcal{L}$ in terms of f can often be found.

Let us consider the example

$$i\,\frac{df(x)}{dx} - f^2(x) = c^2, \quad f(0) = 0, \tag{B5}$$

and suppose we are required to find $f(x_0)$. Writing Eq. (B2) explicitly, we have

$$f_v(x_0) = f_t(x_0) - \int_0^{x_0} dx\,\mathcal{L}_t(x_0,x) \times\left(i\,\frac{df_t(x)}{dx} - f_t^2(x) - c^2\right), \tag{B6}$$

where $f_t(x)$ is chosen so that $f_t(0) = 0$. The usual process of integration by parts leads to the $\mathcal{L}$ equation, which we write in a form slightly different from (B4), taking the δ function into account as a boundary condition:

$$\frac{i\,d\mathcal{L}(x_0,x)}{dx} + 2f(x)\mathcal{L}(x_0,x) = 0, \quad \mathcal{L}(x_0,x_0) = 1. \tag{B7}$$

This immediately admits the solution

$$\mathcal{L}(x_0,x) = \exp\left(2i\int_{x_0}^{x} f(x')\,dx'\right). \tag{B8}$$

An obvious choice for $\mathcal{L}_t$ in Eq. (B6) is the right-hand side of Eq. (B8) with f replaced by f_t. The above example arises in mathematical physics for Riccati-type equations such as the ones that occur in the phase-amplitude method[36] for scattering. The phase function obeys a first-order nonlinear equation similar to Eq. (B5), whereas the amplitude function obeys a linear equation, but one that involves the phase function. In fact, the adjoint function $\mathcal{L}$ in Eqs. (B7) and (B8) is just the square of the amplitude function.[37]

As another example to illustrate the construction of the adjoint function for a nonlinear problem, consider the Lotka-Volterra equations that describe two interacting species[38]:

$$\begin{aligned} \frac{dN_1}{dt} &= \alpha_1 N_1(1 - N_1/\gamma) - \beta_1 N_1 N_2, \\ \frac{dN_2}{dt} &= -\alpha_2 N_2 + \beta_2 N_1 N_2, \end{aligned} \tag{B9}$$

where N_1 and N_2 are functions of t, and α, β, and γ are constants. This problem is in matrix form and one can write $\Xi'\delta N$ as

$$\frac{d}{dt}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \delta N_1 \\ \delta N_2 \end{pmatrix} - \begin{pmatrix} \alpha_1 - \beta_1 N_2 - 2\alpha_1 N_1/\gamma & -\beta_2 N_1 \\ \beta_2 N_2 & -\alpha_2 + \beta_2 N_1 \end{pmatrix}\begin{pmatrix} \delta N_1 \\ \delta N_2 \end{pmatrix}. \tag{B10}$$

$\Xi'^{\dagger}L$ is then, correspondingly

$$-\frac{d}{dt}(L_1 L_2)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - (L_1 L_2)\begin{pmatrix} \alpha_1 - \beta_1 N_2 - 2\alpha_1 N_1/\gamma & -\beta_2 N_1 \\ \beta_2 N_2 & -\alpha_2 + \beta_2 N_1 \end{pmatrix}. \tag{B11}$$

At this stage, the coefficients α, β, γ, and N can be regarded as known and L_i is obtained in terms of them. These examples, and the one considered in Sec. V, illustrate that nonlinear problems can be handled in our general variational formalism in a straightforward manner.

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